The Residual Arsenic Site in Oxidized $Al_xGa_{1-x}As$ (x = 0.96)

X-ray absorption spectroscopy is a unique and powerful technique to isolate contributions from atoms with differing charge states in materials. This advantage has been fully exploited in this study of the passivation of GaAs films to produce gate oxides. The data analysis shows that the residual As in wet-oxidized AlGaAs films is distributed between a mixture of ~80% As^{3+} and ~20% As^{5+} sites that are locally similar to As_2O_3 and As_2O_5.

The III-V semiconductors, such as GaAs, have intrinsic advantages relative to Si for electronic devices. For example, they have lower effective mass, direct gap, and higher electron and hole mobility compared with Si so that III-V semiconductors could be used to produce higher speed and lower power MOSFET. If an oxide equivalent to SiO_2 could be formed from III-V's, passivation layers and high-performance MOSFETs could be made using these materials.

Despite their promise, practical III-V MOSFET devices require a significant improvement in both the quality of the gate oxide and the interface between the oxide and semiconductor, and these material issues have only begun to be explored. Of particular interest is the role of residual As, which is produced as a result of the oxidation. Ashby et al. [1] have shown that the bulk As level and leakage current is reduced through continued heating after complete oxidation, but that partial Fermi-level pinning remains possibly due to interfacial As precipitates. However, in producing these insulating layers, the degree to which, and the form in which, As remains are still unclear. The nature and structure of the oxide interface are also not well understood.

In this work, we present the results of x-ray absorption fine structure spectroscopy (XAFS) studies on the chemical state and site of residual As within the bulk of AlGaAs native oxide films. The XAFS technique [2] is sensitive to the local structure about
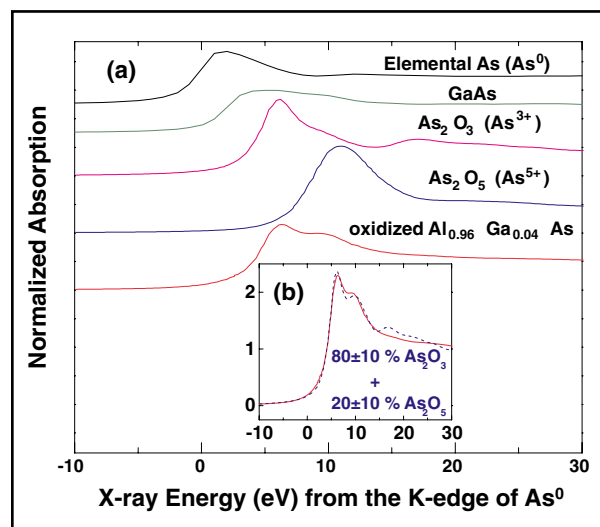

FIG. 1. (a) XANES spectra of the oxide film (oxidized $Al_{0.96}Ga_{0.04}As$) and powders of elemental As, GaAs, As_2O_3 and As_2O_5; (b) oxide film spectra (solid line) compared with a sum of 80% As_2O_3 and 20% As_2O_5 (dotted line).

a chosen atomic species, revealing the types of nearby atoms and the radial distance distributions to these neighbors. By carefully measuring the XAFS spectra near the absorption threshold, x-ray absorption near-edge structure (XANES) can also often be used to determine formal charge state and site symmetry [3].

The sample used for this study is grown by molecular beam epitaxy on semi-insulating GaAs and consists of a 7000 Å GaAs buffer layer, 5000 Å $Al_xGa_{1-x}As$ (x ~ 0.96), and a 200 Å GaAs cap layer. After selectively removing the GaAs cap, the sample

is loaded into a quartz tube furnace (400°C) and the AlGaAs layer oxidized as a carefully controlled amount of water vapor and nitrogen gas are introduced into the furnace. To study the As specifically in the oxide film in isolation of the GaAs substrate, the sample is subsequently mounted oxide-down on a glass slide using low-temperature wax, and the substrate is chemically removed.

The XAFS measurements about the As K-edge are performed at the Advanced Photon Source (APS) using the Materials Research Collaborative Access Team (MR-CAT) undulator beamline [4]. The XAFS data were obtained by monitoring the x-ray fluorescence from the oxidized $Al_{0.96}Ga_{0.04}As$ film as a function of incident x-ray energy.

The XANES spectra for this work are used to "fingerprint" the As site. The absorption edge (E_0) shifts higher with increasing As oxidation state. For analysis of XANES, the x-ray energy origin is set at 11867 eV (K-edge of As^0). The As K-edge XANES spectra of standard compounds (As^0, GaAs, As^{3+}, and As^{5+}) and the oxidized $Al_{0.96}Ga_{0.04}As$ sample are shown in Fig. 1a. None of these compounds singly matches well with the AlGaAs native oxide. The XANES spectrum of the oxide film shows that the sample contains primarily As^{3+}, with the additional feature at 10 eV indicating the presence of As^{5+} species. The best fit to the spectrum (−10 to 30 eV), shown in Fig. 1b, is obtained from a combination of 80% As_2O_3 and 20% As_2O_5; uncertainties are estimated as ±10% of these values through the use of different fitting ranges.

For the same samples for which near-edge (XANES) analysis is presented above, analysis has also been performed on extended x-ray absorption fine structure (EXAFS) data where energies well beyond the E_0 are considered. The raw data is processed to isolate the fine structure oscillations, $\chi(k)$, which is then Fourier-transformed to a pseudo-radial distribution function in r-space (Å). Major peaks in r-space correspond to atomic shells around the excited As atoms (e.g., As-O and As-As) that backscatter the outgoing photoelectron waves. These spectra are then fit to simulations from the multiple scattering code FEFF6.01, and structural parame-
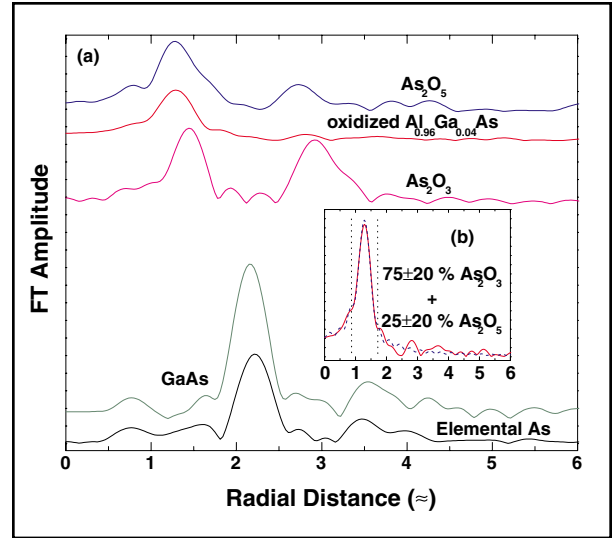

FIG. 2. (a) Magnitudes of the Fourier Transform (FT) of the As K-edge data for the oxide film (oxidized $Al_{0.96}Ga_{0.04}As$), elemental As, GaAs, As_2O_3 and As_2O_5; (b) oxide film data (solid line) with the fit of 71% As_2O_3, 21% As_2O_5 tetrahedral, and 4% As_2O_5 octahedral (dotted line).

ters (interatomic distances, thermal disorders, etc.) are extracted using the program FEFFIT.

In Fig. 2a, the As K-edge EXAFS r-space spectra of the oxidized $Al_{0.96}Ga_{0.04}As$ sample is shown along with spectra from the standard compounds of elemental As, GaAs, As_2O_3, and As_2O_5. Casual inspection indicates that the As atoms in the film are likely to be coordinated with O. The nearest neighbor distances of elemental As (As-As: 2.52 Å), and GaAs (As-Ga: 2.45 Å), as shown in Fig. 2a, as well as AlAs (As-Al: 2.45 Å), are far from the peaks of oxidized $Al_{0.96}Ga_{0.04}As$ data.

However, our XANES analysis suggests that the residual As is distributed ~80% to As^{3+} and ~20% to As^{5+} sites in the oxide sample. Thus, for an independent EXAFS analysis, we have fit the r-space EXAFS data of oxidized $Al_{0.96}Ga_{0.04}As$ to those calculations for the three first shells (one As_2O_3 site and two As_2O_5 sites; As_2O_5 has both tetrahedral and octahedral sites). The best data fit, shown in Fig. 2b, is obtained by a combination of 75% As_2O_3, 21% As_2O_5 tetrahedral site, and 4% As_2O_5 octahedral site. Conservatively estimated uncertainties are ±20% of these values. A large Debye-Waller factor (>0.01 $Å^2$) for the As_2O_5 octahedral site results when the two As_2O_5 sites are decoupled, further indicating that the

As_2O_5 octahedral site contribution is negligible in the EXAFS data fitting.

Comparing the oxidized $Al_{0.96}Ga_{0.04}As$ data in Fig. 2 with that of the crystalline As_2O_3 and As_2O_5 standards, the essential lack of higher shell scattering features indicates larger disorder and suggests that the residual As in $Al_{0.96}Ga_{0.04}As$ converts to an amorphous matrix of As_2O_3 and As_2O_5 during the wet oxidation process. Our EXAFS analysis is consistent with the independent XANES analysis of Fig. 1 within uncertainty limits, and both indicate that less than 10% (estimated detection limit) of the As atoms in the oxide film are at any of the considered sites except for As_2O_3 and As_2O_5.

In summary, both EXAFS and XANES analyses show that the residual As in wet-oxidized AlGaAs films is distributed between a mixture of ~80% As^{3+} and ~20% As^{5+} sites that are locally similar to As_2O_3 and As_2O_5. To be consistent with our data, less than about 10% of the As atoms can be in elemental As, GaAs, or in interstitial or substitutional sites in Al oxides or Al hydroxides. This is good news for the use of these materials for electronic devices: Unlike As or GaAs precipitates, the As oxides do not contribute to electrical leakage through the layer.

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